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(54) Title: IMPROVED METHOD FOR BLEACHING LIGNOCELLULOSIC PULP (57) Abstract The present invention is directed to a method for treating lignocellulosic pulp prior to a bleaching step to minimize consumption of bleaching agent during the bleaching step which comprises the steps of (a) contacting the lignocellulosic pulp with an aqueous solution having a pH of at least about 5 and less than about 11 for a time sufficient to dissolve lignin from the pulp to form a reduced-lignin pulp and a lignin-rich solution, (b) separating the reduced-lignin pulp from the lignin-rich solution, and (c) bleaching the reduced-lignin pulp with the bleaching agent; wherein the time sufficient to dissolve lignin from the pulp to form a reduced-lignin pulp and a lignin-rich solution in step (a) is an amount of time which results in a decrease in bleaching agent consumption in step (c) in the range from about 10 % to about 20 %.		

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IMPROVED METHOD FOR BLEACHING LIGNOCELLULOSIC PULP

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Field of the Invention

This invention pertains to improved methods for bleaching lignocellulosic pulp. More particularly, this invention pertains to methods for treating lignocellulosic pulp prior to a bleaching step to minimize consumption of the bleaching agent. The method comprises contacting the lignocellulosic pulp with an aqueous solution having a pH of at least about 5 and less than about 11 for a time sufficient to dissolve lignin from the pulp to form a reduced-lignin pulp and a lignin-rich solution, separating the reduced-lignin pulp from the lignin-rich solution, and bleaching the reduced-lignin pulp with the bleaching agent.

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Description of the Background

Wood is composed of two main components - a fibrous carbohydrate or holocellulosic component and a non-fibrous component called lignin. Holocellulose is composed of about 70% alkali-insoluble *alpha*-cellulose and about 30% alkali-soluble hemicellulose. The non-fibrous lignin component is a three-dimensional polymeric material consisting mainly of phenylpropane units.

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For use in paper-making processes, wood must be converted to pulp. During chemical pulping, the cellulosic fibers are separated from one another in a manner to preserve the inherent fiber strength and to remove as much lignin as possible. In a chemical pulping process, wood is digested with chemical solutions to solubilize and remove a portion of the lignin. Examples

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of chemical pulping procedures are the soda (sodium hydroxide), sulfite, and kraft processes.

5 The basic and modified kraft processes are the principle chemical processes utilized in paper manufacturing because these processes do not significantly degrade the cellulosic component of the wood. The basic kraft process involves digesting wood chips in an aqueous solution of sodium hydroxide and sodium sulfide to form a high strength pulp. The basic kraft process is described in detail in *Handbook for Pulp & Paper Technologists*,
10 Chapter 7, Kraft Pulping (TAPPI, U.S.A.).

 The modified kraft processes are even milder than the basic kraft process on the cellulosic component and yield even higher strength pulp. The modified kraft processes, also known as "extended delignification" pulping
15 processes, either involve adding the pulping chemicals in a specific sequence, adding the pulping chemicals at different locations in the digestion apparatus, adding the pulping chemicals at different time periods, or removing and reinjecting liquors in a prescribed sequence to remove lignin and reduce attack on the cellulosic fibers. The kraft-AQ process involves adding small amounts
20 of anthraquinone to the pulping liquor to accelerate delignification and limit attack upon the cellulosic fibers. A variety of additional extended delignification techniques are known in the art and include Kamyr Modified Continuous Cooking (MCC), described by V.A. Kortelainen and E.A. Backlund in *TAPPI*, vol. 68 (11), 70 (1985); Beloit Rapid Displacement Heating (RDH),
25 described by R.S. Grant in *TAPPI*, vol. 66 (3), 120 (1983); and Sunds Cold Blow Cooking, described by B. Pettersson and B. Ernerfeldt in *Pulp and Paper*, vol. 59 (11), 90 (1985).

 The pulp formed after digestion of the wood is generally a dark
30 colored slurry of cellulosic fibers known as "brownstock". The dark color of the brownstock is caused by chromophoric groups in the lignin remaining in the pulp formed during the digestion period. This dark lignocellulosic pulp may be used directly in the paper making operation if paper color is not important or may be bleached to a brightness consistent with the planned utilization of the
35 pulp. Prior to bleaching, the pulp is generally transferred to a blow tank to relieve pressure and to separate the pulp material as a fibrous mass. The fibrous mass is then washed to remove residual chemicals and soluble materials such as lignin degradation products.

To lighten the color of the brownstock pulp and make it suitable for use in printing, writing, or other white paper applications, the lignin remaining in the pulp must be chemically removed or converted into colorless compounds by bleaching or brightening. Pulp bleaching is generally a multi-stage process employing chlorine-containing compounds such as calcium hypochlorite, sodium hypochlorite, elemental chlorine, or chlorine dioxide. Bleaching of lignocellulosic pulp using chlorine containing compounds is well known in the art and is discussed in detail in United States patent no. 1,957,937, issued to *Campbell et al.*; United States patent no. 2,975,169, issued to *Cranford et al.*; United States patent no. 3,462,344, issued to *Kindron et al.*; and *Handbook for Pulp and Paper Technologists*, Chapter 11: Bleaching (11.3) (TAPPI, USA).

The following letter codes will be used to describe chemical reactants and process steps employed in paper making.

5	C =	Chlorination	Reaction with elemental chlorine in acidic medium.
	E =	Alkaline Extraction	Dissolution of reaction products with NaOH.
10	E ₀ =	Oxidative Alkaline Extraction	Dissolution of reaction products with NaOH and oxygen.
	D =	Chlorine Dioxide	Reaction with ClO ₂ in acidic medium.
	P =	Peroxide	Reaction with peroxides in alkaline medium.
15	O =	Oxygen	Reaction with elemental oxygen in alkaline medium.
	O _m =	Modified Oxygen	Alkali treatment of low to medium consistency pulp followed by reaction of high consistency pulp with oxygen.
20	Z =	Ozone	Reaction with ozone.
	Z _m =	Modified Ozone	Uniform reaction with ozone.
	C/D =		Admixtures of chlorine and chlorine dioxide.
25	H =	Hypochlorite	Reaction with hypochlorite in alkaline solution.

Although chlorine and chlorine containing compounds are effective bleaching agents, chlorine is difficult to handle and is hazardous to personnel and machinery. Furthermore, the effluents from chlorine bleaching processes contain large amounts of chloride by-products which readily corrode

paper making equipment and chlorinated compounds which can pose environmental concerns. Chloride ion build-up prevents the recycling of washer filtrate in a closed system operation unless expensive recovery operations are employed.

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As a consequence, chlorine-containing bleaching agents have been replaced with non-chlorine-containing bleaching agents such as oxygen and hydrogen peroxide. The use of oxygen permits the recycling of the effluent and permits a substantial reduction in the amount of elemental chlorine used. A number of processes for bleaching and delignifying pulp with oxygen have been proposed, such as those described in United States patent no. 1,860,432, issued to *Richter*, United States patents nos. 2,926,114 and 3,024,158, issued to *Grangaard et al.*, United States patent no. 3,274,049, issued to *Gaschke et al.*, United States patent no. 3,384,533, issued to *Meylan et al.*, United States patent no. 3,251,730, issued to *Watanabe*, United States patent no. 3,432,282, issued to *Rerolle et al.*, United States patent no. 3,661,699, issued to *Farley*, United States patent no. 4,619,733, issued to *Kooi*; and P. Christensen in "Bleaching of Sulphate Pulp with Hydrogen Peroxide", *Norsk Skogindustri*, 268-271 (1973). Alkaline pretreatment of pulp prior to oxygen delignification is suggested by United States patent no. 4,806,203, issued to *Elton* and United States patent no. 5,085,734, issued to *Griggs*. A method using oxygen as a first stage bleaching agent to solubilize a major amount of lignin and chlorine as a second stage bleaching agent to remove the remaining lignin is described by P. Christensen, "Bleaching of Sulphate Pulp with Hydrogen Peroxide", *Norsk Skogindustri*, 268-271 (1973).

The use of oxygen as a bleaching agent is not, however, completely satisfactory. For example, oxygen is not as selective a delignification agent as elemental chlorine and only a limited number of oxygen delignification reactions can be carried out until the cellulosic fibers are attacked. In addition, the lignin remaining after oxygen delignification has typically been removed by chlorine bleaching to obtain a fully-bleached pulp using reduced amounts of chlorine. Even at reduced chlorine concentrations, however, the corrosive chloride by-products soon reach unacceptable concentration levels in a closed cycle operation.

Ozone has also been used as a bleaching agent for pulp. The exceptional oxidative properties of ozone and its relatively high cost, however, have in the past limited the development of satisfactory ozone bleaching

processes. Ozone readily reduces the lignin in pulp but it also aggressively attacks the cellulosic fibers to reduce the strength of the pulp. The reactivity and stability of ozone is also extremely sensitive to reaction conditions such as pH changes.

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United States patent no. 2,466,633, issued to *Brabender et al.*, describes a bleaching process wherein ozone is passed through a pulp having a moisture content of between about 25% and about 55% and a pH in the range from 4 to 7. *N.Liebergott*, "Paprizone Treatment, A New Technique for Brightening and Strengthening Mechanical Pulps" describes a single stage bleaching process which combines peroxide and ozone in a synergistic combination to brighten and strengthen mechanical pulp. United States patent no. 4,196,043, issued to *Singh*, discloses a multi-stage bleaching process characterized by from one to three ozone bleaching stages and a final treatment with alkaline hydrogen peroxide, each stage being separated by an alkaline extraction. United States patent no. 4,283,251, issued to *Singh*, discloses the use of a low consistency acidic retention treatment located between an ozone bleaching treatment and an alkaline treatment. United States patent no. 4,080,249, issued to *Kempf et al.*, discloses a method for bleaching pulp having a consistency between about 1% and about 10% and a pH between about 1 and about 7 with a very finely divided stream of ozone in a highly agitated system. Canadian patent no. 1,112,813, issued to *Kempf*, describes an ozone bleaching method wherein the pH of a pulp slurry of less than 5 after ozone treatment is adjusted to between 6 and 9 to facilitate alkaline extraction of oxidized lignin. United States patent no. 4,372,812, issued to *Phillips et al.*, discloses a multi-stage bleaching process which comprises an oxygen bleaching step, a peroxide bleaching step, and an ozone bleaching step. United States patent no. 4,468,286, issued to *Johnsen*, discloses a method for bleaching pulp with ozone in a multi-path system.

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United States patent no. 4,278,496, issued to *Fritzvold*, discloses a bleaching process which comprises treating a finely divided pulp with ozone initially at a low pH value then later at a high pH value. The pulp is preferably processed before ozone treatment to a "light and fluffy consistency".

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Liebergott et al., "Bleaching a Softwood Kraft Pulp Without Chlorine Compounds", TAPPI Journal, 76 (August 1984) and *N. Soteland*, "Bleaching of Chemical Pulps With Oxygen and Ozone", *Pulp and Paper Magazine of Canada*, T153-58 (1974) disclose a multi-step bleaching process

wherein lignocellulosic pulp is subjected to an initial oxygen delignification stage followed by a treatment of the partially delignified pulp with a gaseous ozone bleaching agent. Subsequent to the ozone treatment, the pulp is subjected to an alkaline extraction to remove a substantial portion of any remaining lignin and to prevent redeposition upon the pulp of the by-products from the previous reactions. This treatment is then followed by a final bleaching treatment with an alkaline peroxide solution.

Canadian patent no. 1,132,760, issued to *R.B. Phillips et al.*, describes a method using effluents from the next later stage of the bleaching sequence as shower water for the washing step following the preceding stage of the bleaching sequence. The countercurrent washing reduces the amount of fresh water needed in a multi-stage bleaching process and permits reuse of the various effluents in a substantially closed cycle bleaching process. The countercurrent washing also reduces solubilized compounds associated with the pulp so that the ozone is primarily and productively consumed in bleaching the pulp and not significantly consumed by side-reactions.

Laxen, International Pulp Bleaching Conference, Stockholm, June 1991, pp. 19-31, describes a medium consistency bleaching step carried out at pH 5 to avoid lignin precipitation.

Despite efforts carried out in this area, no satisfactory commercial high-consistency process for the manufacture of ozone bleached lignocellulosic pulp from softwood and related pulp, especially southern softwood, has been disclosed. Accordingly, improved methods for bleaching lignocellulosic pulp requiring reduced amounts of bleaching agent such as methods for separating residual lignin from pulp before bleaching the pulp and methods reusing the effluents in the bleaching process are highly desirable. The present invention provides such novel bleaching methods without the disadvantages characteristic of previously known methods.

SUMMARY OF THE INVENTION

The present invention is directed to a method for treating lignocellulosic pulp prior to a bleaching step to minimize consumption of bleaching agent during the bleaching step which comprises the steps of (a)

contacting the lignocellulosic pulp with an aqueous solution having a pH of at least about 5 and less than about 11 for a time sufficient to dissolve lignin from the pulp to form a reduced-lignin pulp and a lignin-rich solution, (b) separating the reduced-lignin pulp from the lignin-rich solution, and (c) bleaching the reduced-lignin pulp with the bleaching agent; wherein the time sufficient to dissolve lignin from the pulp to form a reduced-lignin pulp and a lignin-rich solution in step (a) is an amount of time which results in a decrease in bleaching agent consumption in step (c) in the range from about 10% to about 20%.

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BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a schematic diagram illustrating the pulping, oxygen delignification, and ozone delignification/bleaching steps of the process of the invention.

Figure 2 is a schematic diagram illustrating the pH values of the effluents and wash liquor between an O (reaction with oxygen in alkaline medium) and a Z (reaction with ozone) stage of a delignification process.

Figure 3 is a schematic diagram illustrating the alkaline extraction and peroxide bleaching stages.

Figure 4 is a graph illustrating the effect of the pH of the wash water on ozone consumption by organic solids in a delignification/bleaching process at a production rate of 1000 air dried tons of pulp per day.

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DETAILED DESCRIPTION OF THE INVENTION

Applicants have discovered an improved method for bleaching high consistency lignocellulosic pulp which minimizes the unproductive consumption of bleaching agent. The novel method involves removing a significant amount of residual lignin from the pulp prior to the bleaching step to maximize bleaching efficiency. Applicants have found that at a pH of less than about 5, the lignin in a pulp slurry is substantially a solid

which cannot be easily removed from the pulp. At a pH of about 5 or greater, the lignin dissolves in the slurry and can be easily separated from the pulp by washing or pressing. Removing residual lignin from the pulp greatly minimizes unproductive bleaching agent consumption in the subsequent bleaching stage.

5 The solution containing the dissolved lignin from the press or wash stage can be filtered through a reverse osmosis (RO) or ultra filtration membrane (UF) to produce a permeate solution having a decreased amount of dissolved lignin and a concentrate solution having an increased amount of dissolved lignin. The permeate solution can be recycled into a delignification process or bleaching
10 process. The concentrate solution can be recycled to the recovery boiler or otherwise disposed of. The method of the invention may be employed prior to any bleaching step and preferably is used in combination with a multi-step delignifying and bleaching process which includes the steps of pulping, oxygen delignification, ozone delignification/bleaching, alkaline extraction, and a
15 second or final bleaching with a bleaching agent such as chlorine dioxide or a peroxide. The bleaching steps may include acidification, chemical addition, and the like, to increase the efficiency of consumption of the bleaching agent. Preferably, at least portions of the effluents from the multi-step delignifying and bleaching steps are recycled to the pulp slurry and the pH adjusted to effectively
20 remove residual lignin from the pulp. The present invention minimizes unproductive bleaching agent consumption and maximizes bleaching of the pulp with significant cost savings.

In one embodiment, the process further comprises the step of
25 pulping a lignocellulosic material. The pulping step may be Kraft pulping, Kraft-AQ pulping, or extended delignification. If the process includes a pulping step, at least a portion of the permeate solution from reduced-lignin pulp separation step can be recycled to (a) the pulping step, (b) the slurry forming step for use as a portion of the aqueous solution, or (c) the bleached pulp
30 washing step.

In another embodiment, the process further comprises the step
of delignifying the pulp with oxygen prior to bleaching the pulp by contacting the pulp with an alkaline material and oxygen for a sufficient time and at a
35 sufficient temperature to partially delignify the pulp. In this embodiment, the oxygen treatment of the pulp can comprise combining the pulp at low consistency with an alkaline material and increasing the consistency of the pulp by removing pressate to form a high consistency pulp having a desired amount of alkaline material distributed uniformly throughout and subjecting the high

consistency pulp to oxygen delignification. Preferably this embodiment also comprises filtering the solution to remove a substantial amount of the dissolved organic substances to form a permeate solution and recycling at least a portion of the permeate solution to the oxygen delignification step or the bleached pulp washing step.

In still another embodiment, the process further comprises the steps of treating the bleached pulp with an alkaline solution to dissolve a portion of any remaining lignin to form a treated pulp and a lignin-rich alkaline solution. The treated pulp is then separated from the lignin-rich alkaline solution and at least a portion of the lignin-rich alkaline solution can be filtered to produce a permeate solution having a decreased amount of lignin and a concentrate solution having an increased amount of lignin. The alkaline solution can be filtered through an ultra filtration membrane or a reverse osmosis membrane. At least a portion of the permeate solution can be recycled to the slurry forming step, the bleaching step, or an oxygen delignifying step.

In still another embodiment, the process further comprises bleaching the bleached/delignified pulp to a desired GE brightness and washing the bleached pulp. The second or final bleaching step may utilize a bleaching agent such as a peroxide or chlorine dioxide to bleach the pulp. If chlorine dioxide is used as the bleaching agent, at least a portion of the effluent from the bleached pulp washing step can be filtered to remove dissolved organic and inorganic solids to form a reduced-organic and chloride ion solution. The effluent from the bleached pulp washing step can be filtered through an ultra filtration membrane or a reverse osmosis membrane. At least a portion of the reduced-organic and chloride ion solution can be recycled to the slurry forming step, the bleaching step, or an oxygen delignifying step.

The woods which may be employed in the present invention include both hardwoods and softwoods. In one embodiment, the lignocellulosic pulp is prepared from a hardwood. In another embodiment, the lignocellulosic pulp is prepared from a softwood. Preferably, the lignocellulosic pulp is prepared from a softwood. More preferably, the lignocellulosic pulp is prepared from pine. Most preferably, the lignocellulosic pulp is prepared from kraft/AQ-O pine feedstock or preferably from kraft/O_m pine feedstock. In yet another embodiment, the lignocellulosic pulp is prepared from a mixture of hard and softwood.

The lignocellulosic pulp, both in the bleaching step and in the oxygen delignifying step prior to the bleaching step, is preferably a pulp having a high consistency. High consistency delignification and bleaching is more efficient than medium consistency delignification and bleaching because high consistency reactions contain less water in which a reactant must diffuse to contact the pulp. In a preferred embodiment, the consistency of the pulp in an ozone bleaching step is from about 20% to about 65%, more preferably from about 28% to about 55%, and most preferably from about 35% to about 48%. In another preferred embodiment, the consistency of the pulp in an oxygen delignifying step is from about 25% to about 35%, and more preferably from about 27% to about 28%.

The lignocellulosic pulp in the present invention may be a chemical pulp or a mechanical pulp. Preferably, the lignocellulosic pulp is a chemical pulp.

In accord with the present invention, the lignocellulosic pulp is contacted with an aqueous solution having a pH of at least about 5 and less than about 11, preferably from about 5 to about 10, and more preferably from about 6 to about 9.5. The pH value of the aqueous solution should be at least about 5 to avoid lignin condensation and precipitation and maintaining conditions that promote dissolution.

The amount of time the lignocellulosic pulp is contacted with an aqueous solution having a pH of at least about 5 and less than about 11 is a time sufficient to dissolve lignin from the pulp to form a reduced-lignin pulp and a lignin-rich solution. The exact amount of time necessary to contact the lignocellulosic pulp with the aqueous solution having a pH of at least about 5 and less than about 11 may be varied in order to obtain the result desired in the final product and such variations are now within the capabilities of those skilled in the art without the need for undue experimentation.

In general, the amount of time the lignocellulosic pulp is contacted with the aqueous solution having a pH of at least about 5 and less than about 11 is at least about an hour. When the amount of contact time between the lignocellulosic pulp and alkaline aqueous solution is significantly less than about an hour, the amount of lignin removed from the pulp will be unsatisfactory. The amount of time the lignocellulosic pulp is contacted with the alkaline aqueous solution may also be defined in terms of the amount of

decrease in bleaching agent consumption in the subsequent bleaching step. In accord with the method of the present invention, the decrease in total bleaching agent consumption will be from about 10% to about 20%, preferably from about 12% to about 18%, and more preferably from about 14% to about 16%.

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The bleaching agent for the lignocellulosic pulp in step (c) of the present invention is a fast reacting gaseous bleaching agent. In general, the more reactive the bleaching agent employed, the greater the reduction in the bleaching agent requirement of the bleaching reaction and the greater the improvement in the viscosity, strength, and GE brightness of the product pulp. Gaseous bleaching agents are well known in the art and include, for example, ozone, oxygen, and chlorine-containing compounds such as elemental chlorine and chlorine dioxide. The preferred gaseous bleaching agent is ozone. For convenience, ozone will be referred to as the gaseous bleaching agent throughout this specification.

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Throughout this specification, the following definitions will be used. The definitions are based on those found in Rydholm, *Pulping Processes*, Interscience Publishers, 1965, pages 862-863 and TAPPI Monograph No. 27, *The Bleaching of Pulp*, Rapson, Ed., The Technical Association of Pulp and Paper Industry, 1963, pages 186-187.

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The term "consistency", as used herein, means pulp concentration and refers to the amount of pulp fiber in a slurry expressed as a percentage of the weight of the oven dried fiber over the total weight of the fiber and water. The consistency of a pulp will depend upon the type of dewatering equipment used.

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The term "low consistency", as used herein, refers to concentration ranges of pulp up to about 6%, and preferably up to about 5%. Low consistency pulp is a suspension that is pumpable by an ordinary centrifugal pump and is produced using deckers and filters without press rolls.

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The term "medium consistency", as used herein, refers to concentration ranges of pulp between about 6% and about 20%. Below about 15%, medium consistency pulp can be produced by filters. This level of consistency is the consistency of the pulp mat leaving a vacuum drum filter in the brownstock washing system and the bleaching system. The consistency of a slurry from a washer, either a brownstock washer or a bleaching stage washer,

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is about 9% to about 15%. Above about 15%, medium consistency pulp can be produced by press rolls. Rydholm states that the usual range for medium consistency pulp is from about 10% to about 18% and Rapson states the usual range for medium consistency pulp is from about 9% to about 15%. Medium consistency pulp is pumpable by special machinery.

The term "high consistency", as used herein, refers to concentration ranges of pulp between about 20% and about 65%. Rydholm states that the concentration range of high consistency pulp is from about 25% to about 35% and Rapson states that the concentration range of high consistency pulp is from about 20% to about 35%. These high consistency pulps are obtainable only by the use of presses. The liquid phase is largely absorbed by the fibers and the pulp can be pumped only very short distances.

The term "pulping", as used herein, is used in its conventional sense to refer to digestion of lignocellulosic material to form brownstock. Pulping methods include, for example, kraft, the kraft-AQ process, and other forms of extended delignification.

The term "modified kraft process", as used herein, refers to extended delignification processes and all other modified kraft processes with the exception of the kraft-AQ process. The kraft-AQ process has achieved a special status and acceptance in the art and is separately known by that name. The oxygen delignification step following pulping is not an extended delignification method but is rather a first delignification step for bleaching or brightening the pulp.

There are two principal types of measurements to determine the completeness of the pulping or bleaching process. The measurements are referred to as the "degree of delignification" and the "brightness" of the pulp. The degree of delignification is normally used in connection with the pulping process and the early bleaching stages because it is less precise when only small amounts of lignin are present in the pulp such as in the later bleaching stages. The brightness factor is normally used in connection with the bleaching process because it is more precise when only small amounts of lignin are present and the pulp is lightly colored and highly reflective.

There are many methods for measuring the degree of delignification but most are variations of the permanganate test. The normal

permanganate test provides a permanganate number or "K no." which is the number of cubic centimeters of tenth normal potassium permanganate solution consumed by one gram of oven dried pulp under specified conditions. The K no. is determined by TAPPI Standard Test T-214.

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There are also a number of methods for measuring pulp brightness. Pulp brightness is a measure of reflectivity and its value is expressed as a percent of a scale. A standard method for determining pulp brightness is GE brightness (GEB) which is expressed as a percentage of a maximum GE brightness. GE brightness is determined by the TAPPI Official Method T-452.

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A second method for determining pulp brightness is ISO brightness (ISO) which is expressed as a percentage of maximum ISO brightness. ISO brightness is determined by the TAPPI Official Method T-525.

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The viscosity of a wood pulp is a measure of the degree of polymerization of the cellulose chains which make up the individual wood fibers. A standard method for determining pulp viscosity is cupriethylenediamine ("CED") viscosity. CED viscosity, which will be referred to simply as viscosity, is expressed in units of centipoise (cp). Viscosity is determined by the TAPPI Official Method T-230.

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A second method for measuring pulp viscosity is intrinsic viscosity which is expressed in units of dm^3/kg . Intrinsic viscosity is determined by the ASTM Official Method D-1795.

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A typical pulping, delignifying, and bleaching multi-stage process includes the following steps:

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(a) pulping the lignocellulosic material and recovering the pulping chemicals;

(b) washing the pulp to remove chemical residues and residual lignin, and screening the pulp to remove fiber bundles;

(c) delignifying the pulp with alkaline oxygen (*i.e.*, O or O_m);

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(d) washing the partially delignified pulp to remove dissolved organics, screening the pulp, and recycling a portion of the effluent;

(e) chelating and acidifying the pulp to bind metal ions and adjusting the pH level;

(f) thickening the pulp to high-consistency;

(g) contacting the pulp with a gaseous bleaching agent such as ozone (*i.e.*, Z or Z_m) to further delignify and partially bleach the material;

(h) washing the partially bleached pulp and recycling a portion of the effluent;

5 (i) extracting the pulp with alkali to remove residual lignin;

(j) washing the extracted pulp and recycling a portion of the effluent;

(k) contacting the pulp with a second bleaching agent (*i.e.*, D or P) to brighten and bleach the pulp;

10 (l) washing the bleached pulp to obtain a bleached product having a GE brightness from about 70% to about 90%; and

(m) recycling a portion of the effluent from the P bleaching stage or the D bleaching stage.

15 Each of the delignifying and bleaching process steps is described in the following text.

Pulping

20 An optional first stage in the method of the present invention is the pulping step. This step is optional because there is no criticality in how the pulp is formed. Procedures may be utilized which improve the amount of lignin removed from the lignocellulosic material while minimizing the amount of degradation of the cellulose. A pulping step has been described in
25 PCT/US92/00289, the disclosure of which is expressly incorporated herein by reference. As set out in Figure 1, wood chips 2 are introduced into a digester 4 together with a white liquor 6 comprising sodium hydroxide, sodium sulfide and, if desired, an anthraquinone additive. Sufficient white liquor should be introduced into digester 4 to substantially cover the wood chips. The contents
30 of digester 4 are then heated at a temperature and for a time sufficient to allow the liquor to substantially impregnate the wood chips.

The digester 4 produces a black liquor containing the reaction products of lignin solubilization together with brownstock pulp 8. The cooking
35 step is typically followed by sending the pulp to a blow tank 10 and then washing the pulp to remove most of the dissolved organics and cooking chemicals for recycle and recovery. A screening stage (not shown), in which the pulp is passed through a screening apparatus to remove bundles of fibers that have not been separated during pulping, also is used. The brownstock 8 is then

treated in washing units including final washing unit 12 where residual liquor 14 contained in the pulp is removed.

5 Preferably, the Kraft/AQ pulping technique is employed because the anthraquinone additives used aid in removing lignin without causing significant adverse effects upon the strength characteristics of the cellulose. The amount of anthraquinone in the cooking liquor should be at least about 0.01% by weight, based upon the oven dried ("OD") weight of the wood to be pulped, with amounts of from about 0.02% to about 0.1% generally being preferred.

10 Although the Kraft/AQ technique costs more to perform than an unmodified Kraft treatment, the additional cost is at least partially offset by the savings in the cost of chemicals needed for the subsequent oxygen, bleaching (ozone), and peroxide stages.

15 In addition to the Kraft/AQ process, the pulping stage can be carried out using techniques for extended delignification such as the Kamyr MCC, Beloit RDH, and Sunds Super Batch methods. These techniques also remove more of the lignin during cooking without adversely affecting the strength of the cellulose.

20 The pulping stage may be also carried out, if desired, with the use of an unmodified Kraft process. The brownstock pulp which results from the use of this technique is higher in lignin content than that obtained with the Kraft/AQ and extended delignification processes described above.

25

Oxygen Delignification

The next optional stage in the process of the present invention is the oxygen delignification step. The oxygen delignification step involves removal of residual lignin from the brownstock pulp. In one oxygen delignification technique designated "O", the washed pulp is pressed to a high consistency of at least about 25% and an aqueous alkaline solution is sprayed onto the resultant fiber mat to deposit from about 0.8% to about 7% by weight of the alkaline material onto the pulp. The high-consistency alkaline fiber mat

30 is then subjected to oxygen delignification to remove a substantial portion of the lignin from the pulp. Because the procedure is known to result in a substantial decrease in pulp viscosity when used to obtain substantial decreases in K No., i.e., greater than about 50%, it is important to couple this technique with an efficient pulping process, such as Kraft/AQ, extended delignification, or Kraft

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plus extended delignification. The oxygen delignification treatment may be modified to remove increased percentages of the lignin remaining in the brownstock pulp without causing an unacceptable decrease in the viscosity of the pulp. This modified oxygen delignification treatment allows conventional Kraft pulping to be used with such modified oxygen delignification techniques while still obtaining the desired K Nos. and viscosities.

In a preferred process designated "O_m" (m=modified), the brownstock pulp is uniformly treated at low to medium consistency with alkali. The brownstock is maintained at a pulp consistency of less than about 10%, and preferably less than about 5%, by weight. The consistency of the pulp is generally greater than about 0.5%, since lower consistencies are not economical to process. A most preferred consistency range is from about 0.5% to about 4.5%. Thereafter, the consistency of the pulp is raised to at least about 18%, preferably from about 20% to about 35%, and more preferably to about 27%. Thereafter, the high consistency pulp is directed to an oxygen reactor for delignification using conventional conditions.

The advantage of using the O_m process is illustrated by comparing the K Nos. and viscosities obtained using southern softwoods to those obtained with the O process. Using a conventional Kraft pulping procedure and conventional high consistency oxygen ("O") delignification bleaching, the pulp obtained will typically have a K No. of about 12 to about 14 and a viscosity of about 15. This K No. is too large for later delignification using the ozone stage. However, the use of conventional Kraft pulping with the modified high consistency oxygen bleaching results in a pulp having a K No. of less than about 9 while the viscosity of the pulp is maintained above about 12 to about 14.

The values K No. and viscosity are related because the ratio of the change in viscosity to the change in K No., referred to as the "delignification selectivity" of the process is a measure of the efficiency of the O_m technique for removing lignin while maintaining an adequate level of viscosity. The use of the O_m process provides an enhanced degree of selectivity in the delignification as shown by a reduction in K No. of at least about 20% greater compared to that obtained with the use of an "O" stage. The combination of Kraft pulping and O_m oxygen delignification will result in an enhanced delignification selectivity, i.e., a sufficiently low K No. and a sufficiently high viscosity, to permit further delignification and bleaching by

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ozone and peroxide. The O_m oxygen delignification process is more fully disclosed in United States patent no. 5,085,734, the disclosure of which is expressly incorporated herein by reference.

5 Alternatively, the oxygen delignification treatment may be carried out using a two-stage " O_s " (s = split) alkali addition. In this technique, a first amount of alkaline material is applied to pulp at low consistency by combining the pulp with a quantity of alkaline material in an aqueous alkaline solution. The consistency of the pulp is then increased to a high consistency of
10 at least about 18%. Next, a second amount of alkaline material is applied to the high consistency pulp to obtain a total amount of alkaline material applied to the pulp. After this treatment, the pulp is then subjected to oxygen delignification whereby the enhanced delignification selectivities of the O_m process are achieved.

15 While the O_m process is preferred over the standard " O " method, the alternate O_s technique is most preferred because a lower proportion of the alkaline material is applied to the low consistency pulp compared to the O_m process. This lower proportion of alkaline material reduces the amount of
20 alkaline material utilized in mixing chest 18 and also reduces the amount of this material removed via pressate discharge 32 (see below). Splitting the application of the alkaline material between the high and low consistency pulp reduces the alkali loss in pressate discharge 32 which reduces the amount of alkaline material which must be reintroduced. Further the high consistency
25 alkaline treatment portion of the O_s method permits rapid modification of the amount of the alkaline material present in the pulp entering the oxygen delignification reactor to compensate for changes in the properties (i.e., wood type, Kappa or K No., and viscosity) of the incoming brownstock, or to vary the degree or extent of oxygen delignification for a particular pulp. Other
30 oxygen delignification treatments may be conducted on low or medium consistency pulp but such treatments are generally not preferred.

 As set out in Figure 1, washed brownstock 16 is introduced into a mixing chest 18 where it is uniformly treated with sufficient alkaline
35 material 20 for a time sufficient to distribute a first amount of alkaline material throughout the pulp. The low consistency treatment portion of this O_s process is carried out in the same manner as the O_m process, but less alkaline material (i.e., about half as much) may be applied to the pulp. In the O_m process, an aqueous sodium hydroxide solution is combined with the low consistency pulp

in an amount sufficient to provide essentially the same amounts on the OD pulp as is achieved by the O process. In the O_s process, at least about 0.4% to about 3.5% by weight of sodium hydroxide is deposited on the pulp, based on oven dry pulp after thickening, with the balance applied to the high consistency pulp.

5 Other alkali sources having equivalent sodium hydroxide content can also be employed instead of sodium hydroxide, if desired. Oxidized white liquor is a convenient plant stream which may be utilized.

The alkaline treated pulp 22 is forwarded to a thickening unit

10 24 such as a dewatering press where the consistency of the pulp is increased to the desired value. The pulp consistency increasing step also removes residual liquid or pressate 26. A portion 28 of this pressate 26 may be directly recycled back to brownstock washer 12. Alternately, a portion 30 may instead be directed to mixing chest 18 for use in the low consistency pulp alkaline

15 treatment step. Since the consistency of the pulp is increased in the thickening unit 24, a certain amount 32 of pressate may continually be discharged to the plant liquid recovery system to maintain water balance in the mixing chest 18.

Additional alkaline material 36 is applied to the high

20 consistency brownstock 34 produced by the thickening unit 24 to obtain the desired total amount of alkaline material on the pulp prior to oxygen delignification. This total amount of alkaline material is selected to achieve the desired extent of delignification in the subsequent oxygen delignification step which is carried out on the alkaline material treated high consistency pulp. The

25 total amount of alkaline material actually applied onto the pulp will generally be between about 0.8% and about 7% by weight based on oven dry ("OD") pulp, and preferably between about 1.5% and about 4% for southern softwood, and between about 1% and about 3.8% for hardwood. About half these amounts are preferably applied in each of the low consistency and high consistency

30 treatments. Thus, from about 0.4% to about 3.5%, by weight, preferably from about 0.5% to about 1.9% for hardwood, and from about 0.75% to about 2% for softwood is applied onto the pulp during each of the low and high consistency alkaline treatments. Further details concerning the split addition "O_s" process are set forth in United States patent no. 5,173,153, the disclosure

35 of which is expressly incorporated herein by reference.

The alkaline treated pulp 38 is then forwarded to the oxygen delignification reactor 40 where it is contacted with gaseous oxygen 42. Suitable conditions for oxygen delignification according to either the O, O_m, or

O₃ processes comprise introducing gaseous oxygen at about 80 psig to about 100 psig to the high consistency pulp while maintaining the temperature of the pulp between about 90° C and about 130° C. The average contact time between the high consistency pulp and the gaseous oxygen ranges from about 15 minutes to about 60 minutes.

After oxygen delignification in reactor 40, the partially delignified pulp 44 is forwarded to wash press unit 46 where the pulp is washed with water 48 or filtrate recycled from a subsequent bleaching stage to remove any dissolved organics and to produce high quality, low color pulp 50. A first portion 54 of the oxygen stage wash press unit 46 filtrate 52 can be used to advantage in a first shower on the brownstock washer 12. This step improves washing and reduces the pressate portion 55 which is used in a second shower on washing unit 12 and later returns into the residual liquor 14 which is sent to the plant recovery without further reuse. A second portion 56 of filtrate 52 is discharged directly to the plant recovery system.

After the oxygen delignification stage, the pulp is enhanced because the K No. of the pulp is decreased by at least about 50% compared to a decrease of no more than about 50% with conventional oxygen delignification systems without significantly damaging the cellulose component of the pulp. For the softwood pulp described above, a K No. of about 7 to about 10 and a viscosity of above about 13 is readily achieved. For hardwood pulp, a K No. of about 5 to about 8 and a viscosity above about 13 is obtained after the oxygen delignification step.

Ozone Delignification/Bleaching

A key step in the process of the present invention is ozone delignification/bleaching of the oxygen-delignified brownstock pulp. Treating pulp at high consistencies with ozone without paying attention to the comminution of the pulp fibers or to the contact between the individual fibers and the reactant gas stream invariably results in a non-uniform ozone delignifying of the fibers. Such a non-uniform ozone treatment is designated in the prior art with the letter "Z". While the use of a Z stage is not desirable due to the non-uniformities produced, there are situations where the resulting pulp is useful. However, it is preferred to use a modified ozone technique in which the fibers in a desired size range are uniformly contacted with the ozone gas stream. This ozone treatment is designated "Z_m".

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In accord with the present invention, the pulp is mixed with an aqueous solution to form a slurry having a pH of at least about 5 and less than about 11 for a time sufficient to dissolve lignin from the pulp to form a reduced-lignin pulp and a lignin-rich solution. The reduced-lignin pulp is separating from the lignin-rich solution before bleaching the reduced-lignin pulp with the bleaching agent.

A specific preferred embodiment of the treatment system is schematically shown as 57 in Figure 1 and illustrated in greater detail in Figure 2. The effluents from the alkaline extraction stage washer 111 (see infra), Z washer 106, thickening unit 66 have pH of about 11.5, 6.05, and 1.65, respectively. These effluents are mixed in portions sufficient to result in a wash water of pH 3.7. Fresh water 48 may be added to the wash water to supplement the recycled effluents. The wash water is then used in the last oxygen wash press unit 46 to treat the pulp slurry 44 from the oxygen stage. The pH of the pulp slurry is thereby adjusted from about 10-11 to about 7.3 immediately prior to the ozone delignifying step 101. In the ozone delignifying step, the pulp slurry is adjusted to a pH of about 2 by the addition of acid 60 and the recycle of the acidic effluent 68 from the thickening unit 66 prior to treatment in the ozone reactor 78. This can conveniently be accomplished in a tank.

Thereafter, the pulp is conditioned so as to ensure the most effective selective delignification and to minimize the chemical attack of the ozone on the cellulose. As illustrated in Figure 1, the incoming pulp 50 is directed into a mixing chest 58, where it is diluted to a low consistency. An organic or inorganic acid 60 such as sulfuric acid, formic acid, acetic acid or the like, is added to the low consistency pulp to decrease the pH of the pulp in mixing chest 58 to the range of about 1 to about 4, and preferably from about 2 to about 3.

The acidified pulp is treated with chelating agent 62 to complex any metals or metal salts which may be present. This chelating step is used to render such metals non-reactive or harmless in the ozone reactor so that they will not cause breakdown of the ozone, thus decreasing the efficiency of the lignin removal and also reducing the viscosity of the cellulose. Preferred chelating agents for this ozone treatment, for reasons of cost and efficiency, include diethylenetriamine pentacetic acid ("DTPA"), ethylenediamine

tetraacetic acid ("EDTA"), and oxalic acid. Amounts of these chelating agents ranging from about 0.1% to about 0.2% by weight of oven dry pulp are generally effective, although additional amounts may be needed when high metal ion concentrations are present.

5

The acidified, chelated, low-consistency pulp 64 is introduced into a thickening unit 66, such as a twin roll press, for removing excess liquid 68 from the pulp, wherein the consistency of the pulp is raised to a level above about 20%. At least a portion of this excess liquid 68 may be recycled to mixing chest 58 with a remaining portion 68a being directed to the plant recovery. The resultant high consistency pulp 70 is then passed through compaction device 72 such as a screw feeder which acts as a gas seal for the ozone gas and thereafter through a comminuting unit 74, such as a fluffer, for use in reducing the pulp particle size.

15

A preferred range of consistency, especially for southern United States softwood, is from about 28% to about 50%, with advantageous results being obtained at from about 38% to about 45% prior to contact with ozone. Within the above ranges, preferred results are obtained as shown by the relative amount of delignification, the relatively low amount of degradation of the cellulose, and the noticeable increase in the brightness of the treated pulps.

20

The reaction temperature at which the ozone delignification is conducted is also an important factor in the process of the present invention. The maximum temperature of the pulp at which the reaction should be conducted should not exceed the temperature at which excessive degradation of the cellulose occurs, which with southern United States softwood is a maximum of about 120° F to about 150° F.

25

An important feature of the ozone stage of the invention is that the pulp be uniformly delignified/bleached by the ozone. This uniform delignification is obtained, in part, by comminution of the pulp into discrete floc particles of a size which is of a sufficiently small diameter and of a sufficiently low bulk density so that the ozone gas mixture will completely penetrate a majority of the fiber flocs. Generally, a comminuted pulp particle size of 10mm or less has been found to be acceptable.

30

35

During the ozone delignification process, the particles to be delignified should be exposed to the gaseous ozone delignifying agent by mixing

so as to allow access of the ozone gas mixture to all surfaces of the flocs and equal access by the ozone gas mixture to all flocs. The mixing of the pulp in the ozone gas mixture gives superior results with regard to uniformity as compared to the results obtained with a static bed of flocs which results in channeling wherein some of the flocs are isolated from the ozone gas relative to other flocs and are thereby delignified less than other flocs.

Upon exiting fluffer 74, the oxygen delignified pulp particles 76 enter a reactor apparatus 78 adapted for delignifying these particles from a first GE brightness to a second, higher GE brightness. The pulp fiber particles 76 are delignified by the ozone in reactor 78 typically to remove a substantial portion, but not all, of the lignin. A preferred apparatus comprises a reactor as described in United States patent no. 5,181,989, the disclosure of which is expressly incorporated herein by reference.

As the pulp particles are advanced through this reactor, an internal conveyor 80, preferably in the form of a rotating shaft 82 to which is attached a plurality of paddle members 84, powered by motor 86, is used to provide intimate contact and mixing between the pulp particles and the ozone gas. These conveying means displace and toss the pulp particles in a radial and forward direction while also inducing the ozone to flow and surround the displaced and tossed pulp particles to expose substantially all surfaces of a majority of these particles to the ozone. This step facilitates substantially complete penetration of all surfaces of these particles by the ozone.

At low RPMs, the paddles move the pulp in a manner such that it appears to be "rolling" or "lifted and dropped" through the reactor. At higher RPMs, the pulp is dispersed into the gas phase in the reactor with the pulp particles uniformly separated and distributed throughout the gas causing uniform delignification of the pulp. The overall delignifying rate of the pulp particles is thus significantly improved compared to prior art delignifying methods utilizing fast-reacting gaseous agents such as ozone.

The forward movement of the dispersed pulp approximates plug flow and facilitates a high degree of delignifying uniformity. The reactor is designed to simultaneously control pulp contacting, pulp residence time, and gas residence time while effectively consuming up to 99 percent of the ozone. In this way the pulp is delignified to the desired degree while a preferably high conversion of ozone is achieved.

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5 The ozone gas may be employed as a mixture of ozone with oxygen and/or an inert gas, or it can be employed as a mixture of ozone with air. The amount of ozone which can satisfactorily be incorporated into the treatment gases is limited by the stability of the ozone in the gas mixture. Ozone gas mixtures which typically contain from about 1% to about 8% by weight of ozone in an ozone/oxygen mixture, or from about 1% to about 4% ozone in an ozone/air mixture, are suitable for use in this invention. The ozone gas can be introduced at any position through the outer wall of the shell of the reactor.

10

As shown in FIGURE 1, ozone gas 88 is introduced into the reactor 78 in a manner such that it flows, in one embodiment of the invention, countercurrent to the flow of the pulp.

15

The spent ozone gas 90, as it exits reactor 78, is directed to a carrier gas pretreatment stage 92 where a carrier gas 94 of oxygen or air is added. This mixture 96 is directed to ozone generator 98 where the appropriate amount of ozone is generated to obtain the desired concentration. The proper ozone/air or ozone/oxygen mixture 100 is then directed to reactor vessel 78 for delignification of pulp particles 76.

20

Pulp fiber flocs 102, after treatment, are permitted to fall into tank 104 from which they can be collected and transported to the alkaline extraction and/or bleaching treatment stage described below. Upon completion of the front end of the process, the ozonated pulp, to be acceptable for further treatment, has a brightness of at least about 48, a K No. of less than about 5, and a viscosity above about 9.

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30 A further description and discussion of the reaction conditions utilized in the ozone delignification stage of the invention can be found in United States patent no. 5,188,708, the disclosure of which is incorporated herein by reference. Other ozone delignification treatments may be conducted on low, medium, or high consistency pulp. For example, a high consistency ozone treatment in a moving bed can be used, as disclosed in United States patents no. 3,964,962 and no. 4,278,496. However, these alternative ozone treatments are not preferred.

35

Alkaline Extraction

The next optional step in the process of the present invention is the alkaline extraction of the ozone delignified pulp. In the alkaline extraction step, the pulp from the ozone stage is washed in the Z washer 106 and is then combined with a sufficient amount of alkaline material in the extraction vessel to effect extraction. This is schematically illustrated in Figure 3 where pulp 102 from tank 104 of Figure 1 is transported to the Z washer 106 and then to alkaline extraction vessel 105. The pulp 102 is subjected to an aqueous alkaline solution 103 for a predetermined time and at a predetermined temperature correlated to the quantity of alkaline material to solubilize a substantial portion of any lignin which remains in the pulp. This extraction process also increases the brightness of the pulp, typically by about 2 GE brightness points. Thereafter, the alkali treated pulp is directed to a washing unit and the aqueous alkaline solution is washed from the pulp to remove substantially all of the solubilized lignin from the pulp forming a substantially lignin-free pulp. This step is well known to those skilled in the art. The examples disclosed in United States patent no. 5,188,708 illustrate the preferred extraction parameters for this step of the process. At least a portion of the alkaline solution which is recovered is recycled to a washing unit. Again, major environmental benefits are achieved from the elimination of sewerage of this solution.

Final Bleaching

The next optional step in the process of the present invention is the final bleaching step, which can be performed subsequent to either the ozone delignification step or the alkaline extraction step. This bleaching step can be performed by using peroxide as described in PCT/US92/00289, or chlorine dioxide as described in United States patent no. 5,188,708.

For most paper making processes, a final pulp brightness in the range of about 50 to about 63 GEB, such as that achievable upon completion of the Z_m stage described above, is unsatisfactory. Accordingly, in order to further raise the pulp brightness to a more desirable range of about 75 to about 86 GEB, the substantially delignified pulp from the Z_m stage is subsequently subjected to further bleaching, primarily intended to convert the chromophoric groups on the lignin remaining in the pulp into colorless derivatives. The

preferred bleaching agent is peroxide or chlorine dioxide. The use of both bleaching agents is summarized in the following text.

a. Peroxide Bleaching Agent

5

The consistency and pH of the pulp 102 exiting the ozone stage in Figure 1 must be adjusted prior to carrying out the peroxide bleaching treatment. The consistency is thus raised to a preferred range of from about 10% to about 15% while the pH of the pulp is adjusted upwardly to a final pH
10 from about 9.5 to about 10.5. A peroxide stabilizing agent, selected from sodium silicate, magnesium sulfate, a chelate (such as EDTA or DTPA) or mixtures thereof, is added in an amount sufficient to prevent the undesirable decomposition of the hydrogen peroxide bleaching agent. The preferred stabilizing agent is a mixture of magnesium sulfate and sodium silicate. The
15 stabilizing agents are added on a weight percent basis based upon the weight of the pulp, with preferred ranges of use being up to about 3% of sodium silicate, up to about 0.2% magnesium sulfate, i.e., as magnesium (Mg^{++}), and up to about 0.2% of the chelate.

20

At this stage of the process, several different peroxide bleaching treatments may be selected with the particular one chosen depending on the GEB desired for the final product. In the first instance, a semi-bleached pulp having a final GEB of about 75 can be produced while along an alternative path a final pulp product having a GEB of at least about 83 to about 86 can be
25 produced.

Where a bleached pulp having a final GEB of about 83 to about 86 is desired, a KAQ brownstock pulp is partially delignified with oxygen in accordance with the O_m process and then is further delignified with ozone.
30 The ozonated pulp has a GEB of about 59 to about 65 and is contacted with at least about 0.9%, preferably from about 1% to about 1.5%, and most preferably about 1.1% by weight of a peroxide solution, preferably hydrogen peroxide, based upon the weight of the pulp. The reaction is permitted to continue in a bleaching tower for approximately three hours with no further
35 mixing of the pulp and peroxide once they are initially combined. The pulp must be at a GEB of at least about 59 prior to the peroxide bleaching stage in order to achieve a final GEB of at least about 83.

If, however, the ultimate end use of the pulp produced by the process of the invention requires only a semi-bleached pulp having a final GEB of about 75, the process for forming GEB pulp of 83+ as described above may be modified by reducing the concentration of the peroxide bleaching agent by about 2/3, i.e., to between about 0.20% and about 0.65% and preferably about 0.4%, by weight of the pulp. The pulp is placed in contact with this material (without additional mixing) for about three hours. In order to obtain optimum results with this procedure, the GEB of the ozonated pulp which serves as the starting material must be at least about 59.

In an alternate, but less preferred, process for forming 75 GEB pulp, pulp having an ozone GEB of about 65 is contacted with at least about 0.7% by weight of hydrogen peroxide for a truncated period from about 2 minutes to about 15 minutes, preferably from about 5 minutes to about 7 minutes, in contrast to the three hour interval in the procedure described above, with continuous mixing. At levels of about 0.7 wt % and above of hydrogen peroxide, an increase of about ten points in GEB results from the ozone stage to the peroxide stage. Thus, the ozone stage GEB must be at least about 65 to permit the formation of a semi-bleached pulp of about 75 GEB.

In another method for forming 83+ GEB pulp, the preferred technique combines the truncated process described above (utilizing at least about 0.3% by weight of peroxide) to initially raise the GEB of the pulp by at least about 7 points, and preferably by about 10 points, i.e., to a GEB of about 70 to about 75, followed by tower bleaching this bleached pulp for about three hours (with from about 0.6% by weight peroxide) so as to obtain a final product having a GEB of at least about 83. Thus, the truncated step may be utilized as an initial bleaching stage in the formation of 83+ GEB pulp. An important feature of this preferred process is that the effluent from the final peroxide bleaching stage (i.e., to 83 GEB) is recycled into the ozone delignified pulp prior to the initial bleaching stage. Thus, in the initial stage, not only is the pulp mixed with fresh peroxide, it is also continuously blended with the effluent from the final P-stage. Moreover, before the alkali (i.e., for pH adjustment) and peroxide are added in the final peroxide bleaching stage, the effluent of the initial stage is discharged.

Recycling the effluent from the final bleaching stage to the initial peroxide stage serves two purposes. First, residual peroxide in the bleaching effluent which is recycled may be consumed in the initial stage.

Additionally, recycling the effluent to the initial stage helps to boost the ozone pulp brightness level prior to the final peroxide bleaching stage. As a result, the total amount of fresh hydrogen peroxide required in the bleaching operation is significantly reduced, thus providing an economic advantage tied to the use of the process. Peroxide levels in the effluent discharge are also significantly reduced.

Bleached pulp with a GE brightness of 83+ can also be produced from ozone delignified pulp with a GEB of 55+, i.e., in contrast to the 59+ GEB pulp used in the systems described above. To achieve this result, a Kraft- AQ/O_m or O_s/Z_m pulp is subjected to two consecutive three hour peroxide bleaching treatments, each utilizing at least about 0.9% and preferably from about 1% to about 1.5% of peroxide, by weight, which increases the ceiling brightness by about 4 points and thus provides a sufficient bleaching action to raise the GEB of the pulp from about 55+ to about 83+. As in the systems described above, no extraction is carried out between the ozone and the peroxide stages. One requirement of using this technique, however, is that the pulp, upon exiting the oxygen delignification stage, must have a K No. of 9 or less and a viscosity of at least about 17 cps. This requirement ensures that the pulp retains sufficient strength after oxygen delignification to permit it to withstand the effects of the modified ozone treatment carried out prior to the peroxide bleaching stage.

In one embodiment for forming 70-75 GEB semi-bleached pulp (or alternately, for use in conjunction with an additional subsequent bleaching step to form a pulp having a GEB of at least 83) as set out in Figure 3, ozonated and alkaline extracted pulp 102 is passed through washer 111 to remove the by-products 113 of the alkaline extraction reaction. The washed, alkaline extracted pulp 110 then enters reaction vessel 112 equipped with agitation means such as impeller 114 where it is combined with the hydrogen peroxide bleaching solution 116 for from about 2 minutes to about 15 minutes, and preferably from about 5 minutes to about 7 minutes. Pulp 118 having, for example, a GEB of about 70 to about 75 and an acceptable viscosity of at least about 9 cps, may be removed from reaction vessel 112.

In forming a final pulp product of GEB 83+, one may select as a starting material either 1) ozonized pulp 102a or, 2) partially bleached (i.e., GEB 70-75) pulp 120 from reaction vessel 112. The pulp (102a or 120) is treated with water 122 in (optional) washer 124. Effluent 126 from washer 124

may be recycled to washer 106 in order to conserve the peroxide bleaching agent. Washed pulp 128, having a GEB from about 70 to about 75, is transported at a low consistency, i.e., about 10%, to reactor vessel 130.

5 In vessel 130, pulp 128 is contacted with the peroxide bleaching agent 132 for about three hours and bleached to a GEB of at least about 83. The consistency of bleached pulp 134 is thereafter raised to about 45% by, for example, pressing in a thickening unit such as twin roll press 136. A portion 138 of this pressate is recycled to reaction vessel 112 for use in the
10 initial bleaching treatment significantly reducing the amount of fresh peroxide 116 which must be added. Finally, the high consistency bleached pulp 140 (GEB=83+) is washed with water 142 in washer 144 and the effluent 146 of that wash is discarded by sewerage. Alternately, effluent 146 may be recycled for use in washer 124. The final pulp product 148, having an acceptable
15 viscosity of at least about 9 cps and a GE brightness of at least about 83 may thereafter be collected for use.

b. Chlorine Dioxide Bleaching Agent

20 In accordance with the invention, an appropriate amount of chlorine dioxide (D) enables high-strength pulps having a GE brightness value greater than about 80% to be obtained. Since the pulps entering the chlorine dioxide stage are relatively low in lignin, the chlorine dioxide brightening
25 bleaching can be carried out in the presence of from about 0.25% to about 1% of chlorine dioxide based on the oven dry weight of the pulp.

 The chlorine dioxide which is utilized in the brightening process should preferably be prepared by a process which is free from elemental chlorine. Less preferably, chlorine dioxide which does contain a minor amount
30 of elemental chlorine can be used without any substantial increase in the relative amount of undesirable pollutants because of the relatively low amount of lignin present in the ozone- bleached pulp. The effluent from the final bleaching step of this invention when using chlorine dioxide is exceptionally low and can be discharged safely as shown in Figure 3.

35

 If sewerage of the effluent from the final chlorine dioxide bleaching step is unacceptable, the stream can, however, be further purified by being treated with a membrane filtration process such as reverse osmosis. This technique provides a clean filtrate that can be recycled back to previous

bleaching stages for further use. This has the benefit of reducing fresh water usage. Moreover, the concentrated chloride streams that result from the membrane filtration are relatively low in volume.

5 There may be some cases when extremely high pulp brightnesses are desired, for example, from about 90 to about 92 GEB, where additional stages of bleaching may be required. An additional extraction and chlorine dioxide treatment would be a common choice, thereby creating a O_mZ_mEDED bleach sequence.

10

Throughout this application, various publications have been referenced. The disclosures in these publications are incorporated herein by reference in order to more fully describe the state of the art.

15

Examples

The present invention is further illustrated by the following examples which are not intended to limit the effective scope of the claims. All parts and percentages in the examples and throughout the specification and claims are by weight of the final composition unless otherwise specified.

20

Example 1

25 The following examples are based on mathematical simulations of an OZED process, which process has been described in detail in United States patent no. 5,188,708. The simulation is used to determine the effect of varying the pH of the wash water at the last oxygen stage washer.

30 Conventional techniques for designing wash lines maximize reuse of the acid required in the Z stage and minimize countercurrent recycle of the alkaline E stage filtrate. If none of the alkaline E stage filtrate is recycled to the wash line and only the Z stage effluent is recycled to the oxygen stage washer, the wash liquor would have a pH of about 2.0. The present invention, in contrast, provides a manner for the effluents from the OZED process to be
35 mixed in proportions needed to result in a wash liquor having a pH value from about 6 to about 7. This wash liquor can then be countercurrently recycled to the oxygen stage washer to provide the greatest degree of removal of organic material from the pulp.

Figure 3 and Table 1 summarize the effect of the pH of the wash water on ozone consumption in the pH range from about 2 to about 7.45. The following features were incorporated in the simulation; the displacement of organic material in the pulp was experimentally observed to increase with increasing pH; this displacement was translated into the degree of ozone consumption; and the wash liquor from recycling the effluents was used only on the oxygen stage washer closest to the ozone reactor.

Table 1

Effect of Wash Water pH on Ozone Consumption by Organic Solids
in a 1000 ADTPD Delignification Sequence

Wash Water		Ozone Consumption by Solids	
pH	lb/hr	% organic material on pulp	
2.00	237	0.32	
2.60	230	0.31	
3.00	220	0.30	
4.05	193	0.26	
4.85	175	0.24	
6.00	162	0.22	
7.45	161	0.22	

The results show that at a pulp production rate of 1000 air dried tons of pulp ("ADTPD"), ozone consumption can be decreased by about 1800 pounds per day, if the pH of the wash water for the oxygen stage washer is increased from pH 2 to pH 7.45. This represents a 14% decrease in total ozone consumption. The required capacity of the ozone generators would thus be reduced by about 14%. This represents significant savings in capital and operating expense.

Figure 4 shows that a pH of about 6 results in a significant decrease in ozone consumption. No further benefit is realized by increasing the pH to above about 10 to about 11. Accordingly, the preferred wash solutions have a pH of about 6 to about 8 because of practical considerations regarding the recycling of various effluent streams which are available.

Example 2

Where a final chlorine dioxide bleaching step (D) is performed subsequent to either the ozone delignification or the alkaline extraction steps, it would be desirable to purify the D-stage effluent so that it may be recycled back to previous bleaching stages. This purification, among other benefits, would remove the dissolved chloride ions from the D-stage effluent.

Tests were run to determine the chloride removal capability of ultrafiltration (UF)/reverse osmosis (RO) membrane systems for the treatment of D-stage effluents. Such treatment will allow full countercurrent recycle of effluents from this stage without concern for chloride corrosion problems. In general, ultrafiltration and reverse osmosis membranes are used in series for treating effluent streams containing suspended solids, with the ultrafiltration membrane removing gross contaminants and the reverse osmosis membrane removing ions of interest. The primary purpose of treatment of D-stage effluent is the removal of corrosive chloride ions. Removal of these ions allows full countercurrent recycle of the D-stage effluent with subsequent substantial reductions in overall water use requirements.

Table 2 shows that cellulose acetate membrane is highly effective in removing ionic chlorides from a D-stage effluent. The experiments were carried out at 26° C and 50 bars pressure. The chloride content of the reverse osmosis feed was reduced to 15.9 mg/l in the reverse osmosis permeate, which can thereby be recycled to previous bleaching stages.

Table 2

Stream	Ionic Chloride Content - mg/l
RO Feed	208.7
RO Concentrate	2441.1
RO Permeate	15.9

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10 The invention being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the invention and all such modifications are intended to be included within the scope of the following claims.

We claim

1. A method for treating lignocellulosic pulp prior to a bleaching step to minimize consumption of bleaching agent during the bleaching step which comprises the steps of:

(a) contacting the lignocellulosic pulp with an aqueous solution having a pH of at least about 5 and less than about 11 for a time sufficient to dissolve lignin from the pulp to form a reduced-lignin pulp and a lignin-rich solution;

(b) separating the reduced-lignin pulp from the lignin-rich solution; and

(c) bleaching the reduced-lignin pulp with the bleaching agent; wherein the time sufficient to dissolve lignin from the pulp to form a reduced-lignin pulp and a lignin-rich solution in step (a) is an amount of time which results in a decrease in bleaching agent consumption in step (c) in the range from about 10% to about 20%.

2. The method according to claim 1, wherein the lignocellulosic pulp in step (a) has a consistency from about 20% to about 65%.

3. The method according to claim 2, wherein the lignocellulosic pulp has a consistency from about 28% to about 55%.

4. The method according to claim 1, wherein the lignocellulosic pulp in step (a) is a chemical pulp.

5. The method according to claim 1, wherein the lignocellulosic pulp in step (a) is prepared from a hardwood.

6. The method according to claim 1, wherein the aqueous solution in step (a) has a pH from about 5 to about 10.

7. The method according to claim 6, wherein the aqueous solution has a pH from about 6 to about 9.5.

8. The method according to claim 1, wherein the bleaching agent in step (c) is ozone.

9. The method according to claim 1, further comprising the step of delignifying the lignocellulosic pulp in an oxygen delignification step prior to carrying out step (a).

5 10. The method according to claim 9, wherein the pulp in the oxygen delignification step has a consistency from about 25% to about 35%.

11. The method according to claim 1, wherein the lignocellulosic pulp is prepared from a softwood.

10 12. The method according to claim 11, wherein the lignocellulosic pulp is prepared from pine.

13. The method according to claim 1, wherein at least a portion of the lignin-rich solution in step (b) is filtered to produce a permeate solution having a decreased amount of lignin and a concentrate solution having an increased amount of lignin.

14. The method according to claim 13, wherein the lignin-rich solution is filtered through an ultra filtration membrane or a reverse osmosis membrane.

15 20 15. The method according to claim 13, further comprising a pulping step and an oxygen delignifying step.

25 16. The method according to claim 15, wherein at least a portion of the permeate solution is recycled to a pulping step, an oxygen delignifying step, a slurry forming step, or a bleaching step.

30 17. The method according to claim 1, further comprising a second bleaching step wherein the bleached reduced-lignin pulp in step (c) is bleached with a bleaching agent selected from the group consisting of a peroxide and chlorine dioxide.

35 18. The method according to claim 17, wherein the bleaching agent in the second bleaching step is chlorine dioxide and at least a portion of effluent from the second bleaching step is filtered to remove dissolved solids to form a reduced-organic and chloride ion solution.

19. The method according to claim 18, wherein at least a portion of effluent from the second bleaching step is filtered through an ultra filtration membrane or a reverse osmosis membrane.

5 20. The method according to claim 18, wherein at least a portion of the reduced-organic and chloride ion solution is recycled to slurry forming step (b), bleaching step (c), or an oxygen delignifying step.

10 21. The method according to claim 1, further comprising treating the bleached reduced-lignin pulp in step (c) with an alkaline solution to dissolve a portion of any remaining lignin to form a treated pulp and a lignin-rich alkaline solution and separating the treated pulp from the lignin-rich alkaline solution.

15 22. The method according to claim 21, further comprising filtering at least a portion of the lignin-rich alkaline solution to produce a permeate solution having a decreased amount of lignin and a concentrate solution having an increased amount of lignin.

20 23. The method according to claim 22, wherein at least a portion of the permeate solution is recycled to slurry forming step (b), bleaching step (c), or an oxygen delignifying step.

INTERNATIONAL SEARCH REPORT

International application No.

PC 4/09951

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : D21C 9/147, 9/153, 11/00

US CL : 162/37, 65, 78, 88

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 162/29, 37, 65, 78, 88, 89

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

None

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

None

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X — Y	WO, A, 91/18145 (GRIGGS) 28 November 1991, See Abstract.	1-5, 8, 11, 12, 17-23 ----- 1-23
Y	US, A, 4,279,694 (FRITZVOLD ET AL) 21 July 1981, see Abstract.	9, 10
Y	TAPPI Journal, issued August 1984, LIEBERGOTT ET AL, "Bleaching a Softwood Kraft Pulp Without Chlorine Compounds" see TABLE I.	6, 7

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	* T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be part of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"O" document referring to an oral disclosure, use, exhibition or other means		
"P" document published prior to the international filing date but later than the priority date claimed		

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